



Concentration and Density Changes at an Electrode Surface and the Principle of Unchanging Total Concentration

Stephen W. Feldberg^z and Ernie R. Lewis

Brookhaven National Laboratory, Upton, New York 11973, USA

The principle of unchanging total concentration as described by Oldham and Feldberg [*J. Phys. Chem. B*, **103**, 1699 (1999)] is invoked to analyze systems comprising a redox pair ($X_1^{z_1}$ and $X_2^{z_2}$) plus one or more non-electroactive species ($X_3^{z_3}$, $X_4^{z_4}$... $X_{j_{\max}}^{z_{j_{\max}}}$) where $X_j^{z_j}$ is the j^{th} species with charge z_j and concentration; c_j . The principle states that if the diffusion coefficients for all species are identical and mass transport is governed by the Nernst-Planck expression, the total concentration does not change during any electrochemical perturbation, i.e.: $\sum_{j=1}^{j_{\max}} [X_j^{z_j}] = \sum_{j=1}^{j_{\max}} c_j = S_p$. With this principle we deduce the electrochemically induced difference between the surface and bulk concentrations for each species. Those concentration differences are translated into density differences which are a function of the density of the solvent and of the concentration differences, molecular masses and the standard partial molar volumes of all species. Those density differences in turn can induce convection that will ultimately modify the observed current. However, we did not attempt to quantify details of the natural convection and current modification produced by those density differences. The principle of unchanging total concentration also allows us to suggest experimental ploys that might minimize, if not eliminate, density differences; if there are no density differences there should be no convection save for the possibility of *spontaneous* convection which Amatore, Szunerits, Thouin and Warkocz [*J. Electroanal. Chem.*, **500** 62 (2001)] have identified as a mode of convection that does not depend upon “macroscopic flow or density gradient”. Following the lead of Ngamchuea, Eloul, Tschulik and Compton [*Anal. Chem.*, **87**, 7226 (2015)] we did not consider spontaneous convection in the present work.
© 2016 The Electrochemical Society. [DOI: 10.1149/2.0231604jes] All rights reserved.

Manuscript submitted November 23, 2015; revised manuscript received January 23, 2016. Published February 17, 2016. *This paper is part of the JES Focus Issue Honoring Allen J. Bard.*

The constraint of the *principle of unchanging total concentration* was discussed by Oldham and Feldberg:¹

$$\sum_{j=1}^{j_{\max}} [X_j^{z_j}] = \sum_{j=1}^{j_{\max}} c_j = S_p \quad [1]$$

where c_j (moles cm^{-3}) is the concentration of the j^{th} species at any point (x, y, z) in the solution. This constraint is independent of the charge, z_j , of the j^{th} species. Eq. 1 holds as long as:

- diffusion coefficients of all species are identical.
- electroneutrality obtains throughout the solution (deviations from electroneutrality in the vicinity of the double layer are ignored):

$$\sum_{j=1}^{j_{\max}} c_j z_j = 0 \quad [2]$$

- transport is governed by the Nernst-Planck expression (modified to account for convection if needed):

$$\vec{f}_j = -D\nabla c_j - \frac{F}{RT} D c_j z_j \nabla \Phi \quad [3]$$

where Φ potential at x, y and z , D (cm^2/s) is the common diffusion coefficient, F , R and T have their usual significance; the operator ∇ is defined by:

$$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \quad [4]$$

- solute numbers remain constant.

When these criteria apply, the validity of Eq. 1 is independent of the electrode size and shape and of the electrochemical protocol.

The system of interest for the present work involves an initially present redox moiety $X_1^{z_1}$ at bulk concentration c_1^{bulk} ; the concentration of the complementary redox species $X_2^{z_2}$ will often be zero but need not be. The notational paradigm reserves indexes 1 and 2 for the redox pair and indexes ≥ 3 for any number of additional electroinactive,

charged or uncharged, species: $X_{j \geq 3}^{z_j}$. Bulk concentrations $c_{j \geq 3}^{\text{bulk}}$ are set to meet the condition of electroneutrality (Eq. 2). In principle, species $j \geq 3$ can be neutral with $z_j = 0$ but that case is uninteresting and would produce $c_{j \geq 3, z_j=0}^{x=0} = c_{j \geq 3, z_j=0}^{\text{bulk}}$. In other words: An uncharged non-electroactive species has no effect on the behavior of the system and can be ignored. This will become clearer in later discussion.

The initial boundary condition is consistent with the ratio $c_2^{x=0}/c_1^{x=0} = c_2^{\text{bulk}}/c_1^{\text{bulk}}$. The electrochemical perturbation of the system is that required to reset the ratio $c_2^{x=0}/c_1^{x=0} \Rightarrow \theta_D$ defined by.

$$\theta_D = \frac{[X_2^{z_2}]_{x=0}}{[X_1^{z_1}]_{x=0}} = \frac{c_2^{x=0}}{c_1^{x=0}} \quad [5]$$

Alternatively one can also define α_D (the fraction of conversion of initially present $X_1^{z_1}$ to $X_2^{z_2}$ at $x = 0$):

$$\alpha_D = \frac{\theta_D}{1 + \theta_D} \quad \text{or} \quad \theta_D = \frac{\alpha_D}{1 - \alpha_D} \quad [6]$$

In principle, the value of θ_D (or α_D) could be stepped to any desired new value by changing the electrode potential – easily accomplished if the redox couple is reversible and if there is no significant uncompensated resistance (R_u) – unlikely with low supporting electrolyte. However, R_u can be minimized by clever cell design. Compensating for R_u electronically by positive feedback² is not so easily accomplished since R_u is a function of solution composition which may be changing as a function of time. If the only interest is the limiting case where $\theta_D \Rightarrow \infty$, that can be accomplished rather straightforwardly by setting $E_{\text{applied}} - E^0$ sufficiently positive (for oxidation of $X_1^{z_1}$ to $X_2^{z_2}$ when $z_2 > z_1$) or sufficiently negative (for reduction of $X_1^{z_1}$ to $X_2^{z_2}$ when $z_2 < z_1$).

The objective of the present work is twofold:

1. Invoke the principle of unchanging total concentration to deduce all the surface concentrations $c_j^{x=0}$ (moles cm^{-3}) given the value of θ_D , all the c_j^{bulk} (moles cm^{-3}) values and their associated charges z_j .
2. Use the $c_j^{x=0}$ and c_j^{bulk} values to estimate the difference between the density of the solution at $x = 0$ and the density of the bulk solution.

^zE-mail: feldberg@bnl.gov

This analysis may help to sharpen the distinctions between convection produced by electrochemically induced density gradients and the “spontaneous” convection defined by Amatore et al. as convection that is obtained “in macroscopically immobile solutions (viz., not submitted to any macroscopic flow or any density gradient)”.³ In the present work we do not consider the role of spontaneous convection – for the reasons given by Ngamchuea et al.⁴ who note that the origins of spontaneous convection are difficult to quantify.

In subsequent work Amatore et al.^{5,6} use the words “natural convection” but assume that to be equivalent to “spontaneous convection” as defined above. In the present work we focus on the conditions that produce a density difference between the electrode surface and the solution bulk; we do not attempt to quantify the correlation of the density difference, the density-difference-induced convection and the resultant current modification (see e.g., the recent work of Ngamchuea et al.⁴ and of Sahore et al.⁷

Theory

In the present analysis the *principle of unchanging total concentration* is invoked to deduce all the surface concentrations $c_j^{x=0}$ following a potential induced change in θ_D (or equivalently in α_D) at the electrode surface (see Eq. 6). Heretofore, only the solution for the 3-species problem has been discussed, see e.g. Oldham and Feldberg.¹ For the present analysis we describe a straightforward (albeit iterative) solution to compute $c_{j \geq 2}^{x=0}$ when $j_{\max} \geq 3$. The 3-species problem is a subset of that more complete treatment. The earlier study of the principle evolved from our interest at the time in systems involving little or no added supporting electrolyte. Numerous works have focused on fluxes $D(dc_j/dx)_{x=0}$ as a function of these same variables;^{8–12} however, it is the values of $c_j^{x=0}$ (and not the fluxes) that are of primary interest in the present work because of their relevance to the density of the solution in the depletion region adjacent to the electrode surface. Consequently, we do not attempt to deduce the fluxes (and currents) – they will depend upon the size and shape of the electrode and orientation relative to the gravitational field, time (if the system is not at steady-state) and upon the electrochemical protocol (see e.g. Refs. 4,7).

The 3-species problem.—It is instructive to review first the solution for the 3-species problem which can be solved explicitly.¹ S_P is directly evaluated from Eq. 1:

$$S_P = \sum_{j=1}^3 c_j^{\text{bulk}} \quad [7]$$

It is also the case that (see Eq. 5):

$$\begin{aligned} S_P &= \sum_{j=1}^3 c_j^{\text{bulk}} = c_1^{x=0} + c_2^{x=0} + c_3^{x=0} \\ &= \frac{c_2^{x=0}}{\theta_D} + c_2^{x=0} + c_3^{x=0} = \left(\frac{1}{\theta_D} + 1 \right) c_2^{x=0} + c_3^{x=0} \end{aligned} \quad [8]$$

With rearrangement this becomes:

$$c_3^{x=0} = S_P - \left(1 + \frac{1}{\theta_D} \right) c_2^{x=0} \quad [9]$$

Invoking the electroneutrality constraint and the principle of unchanging total concentration (see Eqs. 2 and 7) leads to:

$$0 = c_1^{x=0} z_1 + c_2^{x=0} z_2 + c_3^{x=0} z_3 = \left(\frac{z_1}{\theta_D} + z_2 \right) c_2^{x=0} + c_3^{x=0} z_3 \quad [10]$$

Then:

$$c_3^{x=0} = - \frac{\left(\frac{z_1}{\theta_D} + z_2 \right)}{z_3} c_2^{x=0} \quad [11]$$

Equating Eqs. 8 and 11 gives

$$S_P = \left(1 + \frac{1}{\theta_D} \right) c_2^{x=0} + c_2^{x=0} \frac{\frac{z_1}{\theta_D} + z_2}{z_3} = c_2^{x=0} \left(\left(1 + \frac{1}{\theta_D} \right) - \frac{\frac{z_1}{\theta_D} + z_2}{z_3} \right) \quad [12]$$

Then:

$$c_2^{x=0} = \frac{S_P}{\left(\left(1 + \frac{1}{\theta_D} \right) - \frac{\left(\frac{z_1}{\theta_D} + z_2 \right)}{z_3} \right)} = \frac{S_P z_3}{z_3 \left(1 + \frac{1}{\theta_D} \right) - \left(\frac{z_1}{\theta_D} + z_2 \right)} \quad [13]$$

$$\begin{aligned} c_1^{x=0} &= \frac{c_2^{x=0}}{\theta_D} = \frac{S_P z_3}{\theta_D \left(z_3 \left(1 + \frac{1}{\theta_D} \right) - \left(\frac{z_1}{\theta_D} + z_2 \right) \right)} \\ &= \frac{S_P z_3}{z_3 (1 + \theta_D) - (z_1 + z_2 \theta_D)} \end{aligned} \quad [14]$$

$$c_3^{x=0} = S_P - (c_1^{x=0} + c_2^{x=0}) = - \frac{S_P (z_1 + \theta_D z_2)}{z_3 (1 + \theta_D) - (z_1 + \theta_D z_2)} \quad [15]$$

The results for two examples of 3-species systems are summarized in Table 1. For example 1A the initially present two species are a singly positively charged redox moiety and its corresponding negatively charged counter ion. For this example, species 2 has zero charge so the redox process is a 1-electron reduction. The species distributions are shown for $\alpha_D = 0.25, 0.5, 0.75$ and 0.999999 . The possibly surprising result is that the final concentration of $c_2^{x=0} = 2c_1^{\text{bulk}}$, a result that has been theoretically explored and discussed along with several other 3-species variations.¹ For the example shown in Table 1B the initial species are the same as for 1A. However, the redox product is now doubly positively charged so the redox process was a 1-electron oxidation.

The general solution for $j_{\max} \geq 3$.—Obtaining the solution for the 3-species problem involved evaluation of three unknowns ($c_1^{x=0}$, $c_2^{x=0}$ and $c_3^{x=0}$) from three equations (Eqs. 1, 2 and 5). For each added species there will be an additional unknown whose evaluation requires

Table 1. Values of $c_j^{x=0}/c_1^{\text{bulk}}$ are computed for some examples of the 3-species problem. Errors are round-off errors associated with double precision computation.

#	j	z_j	$c_j^{\text{bulk}}/c_1^{\text{bulk}}$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.25, \theta_D = 1/3$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.5, \theta_D = 1.0$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.75, \theta_D = 3$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.999999, \theta_D = 1e6$
1A	1	1	1	6/7	2/3	2/5	2e-6
	2	0	0	2/7	2/3	6/5	2
	3	-1	1	6/7	2/3	2/5	2e-6
			$\gamma =$	-0.1542	-0.4054	-0.9163	13.12
1B	1	1	1	2/3	2/5	2/11	6.66667e-7
	2	2	0	2/9	2/5	6/11	2/3
	3	-1	1	10/9	6/5	14/11	4/3
			$\gamma =$	0.1054	0.1823	0.2412	0.2877

an additional equation. When the surface fluxes are zero, as they must be at all times for species $j \geq 3$, and the Nernst-Planck equation (see Eq. 3) leads directly to the Boltzmann relationship for those species:

$$c_{j \geq 3}^{x=0} = c_{j \geq 3}^{\text{bulk}} \exp\left(-\frac{F}{RT} \Phi^{x=0} z_{j \geq 3}\right) = c_{j \geq 3}^{\text{bulk}} \exp(-\gamma z_{j \geq 3}) \quad [16]$$

where:

$$\gamma = \frac{F}{RT} \Phi^{x=0} \quad [17]$$

Eq. 16 can be derived directly from Eq. 3 by setting $\vec{f}_j = 0$ and $\vec{v} = 0$ and considering only a single dimension

$$\vec{f}_j = 0 = -D \frac{dc_j}{dx} - \frac{F}{RT} D c_j z_j \frac{d\Phi}{dx} \quad [18]$$

$$\frac{d \ln[c_j]}{dx} = -\frac{z_j F}{RT} \frac{d\Phi}{dx} \quad [19]$$

Integrating over x from 0 to ∞ assuming that $\Phi^{\text{bulk}} = 0$ and rearranging gives

$$\ln[c_j^{x=0}] - \ln[c_j^{\text{bulk}}] = -\frac{z_j F}{RT} (\Phi^{x=0} - \Phi^{\text{bulk}}) \quad [20]$$

which leads directly to Eq. 16.

The constraints of Eqs. 1 and 2 are now:

$$S_p = \sum_{j=1}^{j_{\max}} c_j^{\text{bulk}} = \sum_{j=1}^{j_{\max}} c_j^{x=0} \quad [21]$$

and

$$\sum_{j=1}^{j_{\max}} c_j^{\text{bulk}} z_j = \sum_{j=1}^{j_{\max}} c_j^{x=0} z_j = 0 \quad [22]$$

Following the approach described in the 3-species model and introducing the boundary condition (Eq. 5):

$$S_p - \sum_{j=3}^{j_{\max}} c_j^{x=0} = c_1^{x=0} + c_2^{x=0} = \frac{c_2^{x=0}}{\theta_D} + c_2^{x=0} = c_2^{x=0} \left(\frac{1}{\theta_D} + 1 \right) \quad [23]$$

Rearranging and introducing the Boltzmann relationship (Eq. 16):

$$c_2^{x=0} = \frac{S_p - \sum_{j=3}^{j_{\max}} c_j^{x=0}}{\left(\frac{1}{\theta_D} + 1 \right)} = \frac{S_p - \sum_{j=3}^{j_{\max}} c_j^{\text{bulk}} \exp[-\gamma z_j]}{\left(\frac{1}{\theta_D} + 1 \right)} \quad [24]$$

Invoking the charge neutrality constraint, Eq. 4, gives:

$$\begin{aligned} 0 &= c_1^{x=0} z_1 + c_2^{x=0} z_2 + \sum_{j=3}^{j_{\max}} z_j c_j^{\text{bulk}} \exp[-\gamma z_j] \\ &= c_2^{x=0} \left(\frac{z_1}{\theta_D} + z_2 \right) + \sum_{j=3}^{j_{\max}} z_j c_j^{\text{bulk}} \exp[-\gamma z_j] \end{aligned} \quad [25]$$

Then

$$c_2^{x=0} = -\frac{\sum_{j=3}^{j_{\max}} z_j c_j^{\text{bulk}} \exp[-\gamma z_j]}{\frac{z_1}{\theta_D} + z_2} \quad [26]$$

Combining Eqs. 24 and 26 gives

$$0 = \frac{S_p - \sum_{j=3}^{j_{\max}} c_j^{\text{bulk}} \exp[-\gamma z_j]}{\frac{1}{\theta_D} + 1} + \frac{\sum_{j=3}^{j_{\max}} z_j c_j^{\text{bulk}} \exp[-\gamma z_j]}{\frac{z_1}{\theta_D} + z_2} \quad [27]$$

or

$$\begin{aligned} 0 &= \left(\frac{z_1}{\theta_D} + z_2 \right) \left(S_p - \sum_{j=3}^{j_{\max}} c_j^{\text{bulk}} \exp[-\gamma z_j] \right) \\ &+ \left(\frac{1}{\theta_D} + 1 \right) \sum_{j=3}^{j_{\max}} z_j c_j^{\text{bulk}} \exp[-\gamma z_j] \end{aligned} \quad [28]$$

When $j_{\max} = 3$, γ can be solved directly. That is easily seen by noting that for $j_{\max} = 3$, Eq. 27 can be written as¹:

$$\begin{aligned} 0 &= \left(\frac{z_1}{\theta_D} + z_2 \right) (S_p - c_3^{\text{bulk}} \exp[-\gamma z_3]) \\ &+ \left(\frac{1}{\theta_D} + 1 \right) z_3 c_3^{\text{bulk}} \exp[-\gamma z_3] \end{aligned} \quad [29]$$

Replacing by $c_3^{x=0}$ (see Eq. 16) and rearranging gives:

$$c_3^{x=0} = -\frac{\left(\frac{z_1}{\theta_D} + z_2 \right) S_p}{z_3 \left(\frac{1}{\theta_D} + 1 \right) - \left(\frac{z_1}{\theta_D} + z_2 \right)} = -\frac{(z_1 + z_2 \theta_D) S_p}{z_3 (1 + \theta_D) - (z_1 + z_2 \theta_D)} \quad [30]$$

Eq. 30 is identical to Eq. 15 directly deduced for the 3-species system. When $j_{\max} > 3$ the value of γ (see Eq. 29) must be obtained iteratively: we used the bisection method¹³ which is relatively easy to implement, e.g., compared to Newton-Raphson method and is adequate for the present purposes. Some sample results are shown in Table II for 5-species and 4-species systems.

A 5-species system allows straightforward examination of what happens when excess electrolyte is present in the system. Initially present in the system will be a redox moiety and its counterion plus a much higher concentration of an additional pair of ions which constitute the supporting electrolyte. The result is that sum of the normalized concentrations of the redox species at $x = 0$ is just what would be expected, i.e.: $c_1^{x=0}/c_1^{\text{bulk}} + c_2^{x=0}/c_1^{\text{bulk}} = 1$. (see Table II). This is definitively not the case when there is no added supporting electrolyte (see Table I). Also shown in Table II are some values of the surface concentrations computed by direct explicit finite-difference simulation.¹¹ We believe that this confirms that the Boltzmann expression, Eq. 16, is producing a correct and unique result.

Summarizing the general solution approach for determining all $c_j^{x=0}$ -values:

1. Solve Eq. 27 for γ (using the bisection method)
2. Given γ : solve Eqs. 24 or 26 for $c_2^{x=0}$
3. Given $c_2^{x=0}$: $c_1^{x=0} = c_2^{x=0}/\theta_D$
4. Given γ and $c_{j \geq 3}^{\text{bulk}}$: solve Eq. 16 for $c_{j \geq 3}^{x=0}$

Estimating and controlling the electrochemically induced density change $\Delta \rho$ at the electrode surface.—In the previous segments we showed that the surface concentrations, $c_j^{x=0}$, for all species can be easily deduced for given values of c_j^{bulk} and θ_D (or, equivalently, α_D) if diffusion coefficients are identical for all species. It is then possible to estimate the difference between the density of the solution at $x = 0$, $\rho^{x=0}$ (g cm^{-3}), and the bulk density, ρ^{bulk} (g cm^{-3}), following an electrochemical perturbation if standard partial molar volumes, β_j ($\text{cm}^3 \text{ moles}^{-1}$), are known and many are.^{14,15} The standard partial molar volume, β_j , is the partial molar volume at infinite dilution. Minimizing density-induced convection would facilitate detection and quantification of Amatore's spontaneous convection.³

Millero¹⁶ has provided the following expression for relative density ρ/ρ^S :

$$\frac{\rho}{\rho^S} = 1 + c_A \left(\frac{M_A}{\rho^S} - \beta_A \right) + S_{V,A} c_A^{3/2} + b_{V,A} c_A^2 \quad [31]$$

M_A (g moles^{-1}) is the molar mass of an ionic solute, A (e.g., KCl), β_A ($\text{cm}^3 \text{ moles}^{-1}$) is the standard partial molar volume, and c_A (moles cm^{-3}) is the concentration (see Millero¹⁶ for definitions of $S_{V,A}$ and

Table II. Values of $c_j^{x=0}/c_1^{\text{bulk}}$ computed for some examples of the 5-species and 4-species systems. Data in parentheses were computed using explicit finite difference simulation and may be subject to small errors of the order of parts per thousand.¹¹ Errors for non-simulated numbers are round-off errors associated with double precision computation.

#	j	z_j	$c_j^{\text{bulk}}/c_1^{\text{bulk}}$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.25, \theta_D = 1/3$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.5, \theta_D = 1.0$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.75, \theta_D = 3$	$c_j^{x=0}/c_1^{\text{bulk}}$ $\alpha_D = 0.999999, \theta_D = 1e6$
2A	1	1	1	0.7500820	0.5000937 (0.50252)	0.2500586	1.00025e-6 (1.6135e-6)
	2	0	0	0.2500273	0.5000937 (0.497680)	0.7501757	1.00025 (1.0003139)
	3	-1	1	0.9998751	0.9997502 (0.99975)	0.9996253	0.9995 (0.9995)
	4	1	1000	1.000125e+3	1.00025e+3 (1.000249e+3)	1.0003749e+3	1.0005e+3 (1.0005e+3)
	5	-1	1000	9.998751e+2	0.99975e+3 (0.99975e+3)	9.99625292	0.9995e+3 (0.9995e+3)
			$\gamma =$	-1.249e-4	-2.498e-4	-3.748e-4	-4.998e-4
2B	1	1	1	0.7500819	0.499844	0.2498714	9.992519e-7
	2	2	0	0.2500273	0.499844	0.7496141	9.99251e-1
	3	-1	1001	1.000875e+3	1.0012499e+3	1.001374e+3	1.001500e+3
	4	1	1000	1.0001249e+3	9.9975039e+2	0.9996257e+3	0.9995011e+3
			$\gamma =$	-1.249e-4	-2.498e-4	-3.744e-4	-4.997e-4

$b_{V,A}$). For the relatively low bulk concentrations likely to be encountered in electrochemical experiments ($< 10^{-3}$ moles cm^{-3}) the terms $S_{V,A}$ and $b_{V,A}$ can be ignored and the following expression is adequately accurate for present purposes:

$$\frac{\rho}{\rho^S} = 1 + c_A \left(\frac{M_A}{\rho^S} - \beta_A \right) \quad [32]$$

Figure 1 compares plots of ρ/ρ^S vs c_A computed using Eqs. 31 (—) and 32 (---) for a variety of single electrolyte solutions.

With the linearity of Eq. 32 and the added presumption that in multispecies systems all moieties behave independently we can modify Eq. 32 to obtain the solution densities at the electrode surface and in the bulk solution, i.e.:

$$\frac{\rho^{x=0}}{\rho^S} = 1 + \sum_{j=1}^{j_{\text{max}}} c_j^{x=0} \left(\frac{M_j}{\rho^S} - \beta_j \right) \quad [33]$$

and

$$\frac{\rho^{\text{bulk}}}{\rho^S} = 1 + \sum_{j=1}^{j_{\text{max}}} c_j^{\text{bulk}} \left(\frac{M_j}{\rho^S} - \beta_j \right) \quad [34]$$

In an electrochemical experiment the difference between the density of the solution at the electrode surface, $\rho_{x=0}$, and the density of the bulk solution, ρ^{bulk} , will initiate convective effects. However, the magnitude of those effects will depend upon many factors, e.g., shape and

size of the electrode, orientation of the electrode relative to the gravitational field, the time-scale of the experiment and the electrochemical protocol (see e.g., the recent work of Ngamchuea et al.⁴ and of Sahore et al.⁷). We only estimate the difference in the relative density, $\Delta\rho/\rho^S$, defined by:

$$\begin{aligned} \frac{\Delta\rho}{\rho^S} &= \frac{\rho^{x=0}}{\rho^S} - \frac{\rho^{\text{bulk}}}{\rho^S} = \sum_{j=1}^{j_{\text{max}}} c_j^{x=0} \left(\frac{M_j}{\rho^S} - \beta_j \right) - c_j^{\text{bulk}} \left(\frac{M_j}{\rho^S} - \beta_j \right) \\ &= \sum_{j=1}^{j_{\text{max}}} G_j (c_j^{x=0} - c_j^{\text{bulk}}) = \sum_{j=1}^{j_{\text{max}}} G_j \Delta c_j \end{aligned} \quad [35]$$

where

$$\Delta c_j = c_j^{x=0} - c_j^{\text{bulk}} \quad [36]$$

and

$$G_j = \frac{M_j}{\rho^S} - \beta_j \quad [37]$$

The G_j -values can be computed from Eq. 37 using known values of the molecular mass, M_j , solvent density, ρ^S , and standard partial molar volumes, β_j , as compiled by Marcus and coworkers.^{14,15} If all G_j -values are identical, i.e.,

$$G_j = G_0 \quad [38]$$

it can be shown that $\Delta\rho/\rho^S = 0$, a result that flows from the principle of unchanging total concentration (Eq. 1). Rearranging Eq. 37 gives:

$$\frac{\Delta\rho}{\rho^S} = G_0 \sum_{j=1}^{j_{\text{max}}} (c_j^{x=0} - c_j^{\text{bulk}}) = G_0 (S_p^{x=0} - S_p^{\text{bulk}}) = 0 \quad [39]$$

Note that it must also be the case (invoking the principle) that

$$\sum_{j=1}^{j_{\text{max}}} \Delta c_j = 0 \quad [40]$$

Thus, in principle, the elimination of the relative density-difference $\Delta\rho/\rho^S$ will occur when all G_j -values are identical assuming, of course, that the prerequisites for the principle of unchanging total concentration are operative, notably that diffusion coefficients of all species are identical. The beauty of this result is that $\Delta\rho/\rho^S = 0$ regardless of the value of θ_D (or equivalently of α_D) and regardless of the electrochemical protocol and mechanism. That means that $\Delta\rho/\rho^S = 0$ even when electron transfer is quasi-reversible or when uncompensated resistance is significant. Nevertheless, establishing the condition that all G_j -values are identical will be a tricky challenge – even with the availability of an impressive compilation of β_j -values for individual ions provided by Marcus et al.^{14,15} β_j -data for neutral

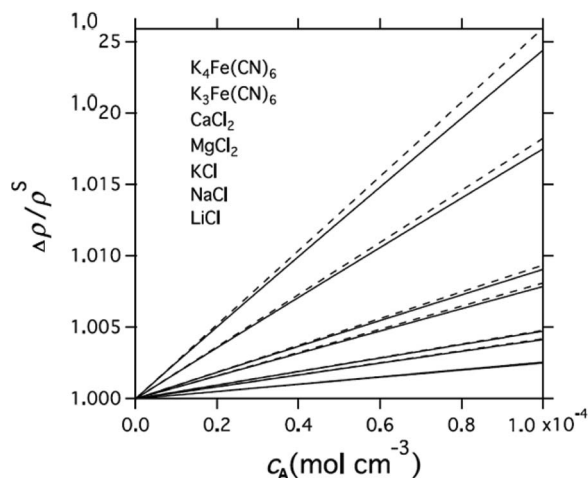


Figure 1. Plots of $\Delta\rho/\rho^S$ vs c_A computed using Eqs. 31 (—) and 32 (---) are compared for a variety of single electrolyte solutions. Electrolyte names from top to bottom correspond to the curve-pairs from top to bottom.

Table III. Simulated values of Δc_j and $\Delta\rho/\rho^S$ computed as a 5-species problem with G_j set equal to M_j values for data of Bond et al.¹² See text for details.

#	j	z_j	c_j^{bulk} (moles cm^{-3})	G_j (cm^3/mole)	Δc_j $\alpha_D = 0.999999, \theta_D = 1e6$
3A	1	-4	1e-6	3541	-1.0e-6
	2	-6	0	3541	7.14286e-7
	3	1	4e-6	452	2.85714e-7
	4	-1	0	126	0
	5	1	0	452	0
					$\Delta\rho/\rho^S = -8.83e-4$
3B	1	-4	1e-6	3541	-1.0e-6
	2	-6	0	3541	7.319717e-7
	3	1	4e-6	452	2.693944e-7
	4	-1	1e-6	126	-6.190130e-8
	5	1	1e-6	452	6.598592e-8
					$\Delta\rho/\rho^S = -8.08e-4$
3C	1	-4	1e-6	3541	-1.0e-6
	2	-6	0	3541	8.243328e-7
	3	1	4e-6	452	1.602377e-7
	4	-1	1e-5	126	-3.851648e-7
	5	1	1e-5	452	4.005943e-7
					$\Delta\rho/\rho^S = -4.17e-4$
3D	1	-4	1e-6	3541	-1.0e-6
	2	-6	0	3541	9.582060e-7
	3	1	4e-6	452	3.444288e-8
	4	-1	1e-4	126	-8.537209e-7
	5	1	1e-4	452	8.610721e-7
					$\Delta\rho/\rho^S = 1.49e-4$
3E	1	-4	1e-6	3541	-1.0e-6
	2	-6	0	3541	9.950978e-7
	3	1	4e-6	452	3.935238e-9
	4	-1	1e-3	126	-9.828425e-7
	5	1	1e-3	452	4.828425e-7
					$\Delta\rho/\rho^S = 3.05e-4$

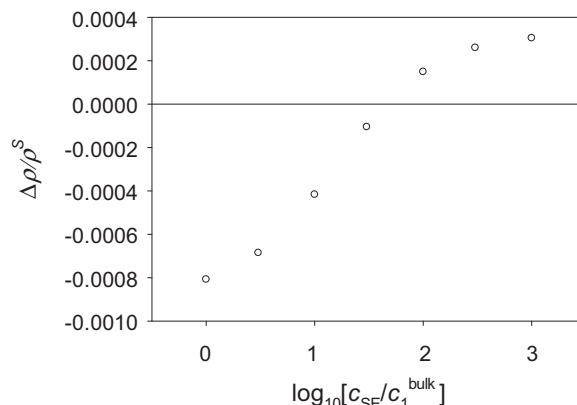
species are sparser (e.g., see Kiselev et al.¹⁷ for β_j -values for ferrocene in a variety of solvents).

Interestingly, there is a plethora of sets of non-identical G_j -values for any given set of j_{max} values of Δc_j which will satisfy

$$\Delta\rho/\rho^S = \sum_{j=1}^{j_{\text{max}}} G_j \Delta c_j = 0 \quad [41]$$

Consider, for example, the data summarized in Table IA for $\alpha_D = 0.999999$: $\Delta c_1 = -1$, $\Delta c_2 = 2$ and $\Delta c_3 = -1$. We have already established that the set of identical G_j -values satisfies Eq. 41. However, it is also easy to see that Eq. 41 will be satisfied when $G_1 = 1$, $G_2 = 2$ and $G_3 = 3$ or more generally when $G_1 = z$, $G_2 = z + y$ and $G_3 = z + 2y$ for any values of y and z . We were surprised to see that these same sets of G_j -values are valid for any value of α_D . That will not be true generally when $j_{\text{max}} > 3$: then the sets of G_j -values effecting $\Delta\rho/\rho^S = 0$ will depend upon the value of α_D and that will compromise the protocol-independence of this analysis when $j_{\text{max}} > 3$. It is also important to remember that a set of non-identical G_j -values which satisfies Eq. 41 will depend upon the number of species involved and upon the mechanistic details. Only the set comprising identical G_j -values will satisfy Eq. 41 for all mechanisms and protocols.

Perhaps the easiest way to reduce, if not eliminate, the density difference and therefore the density-gradient-induced convection, is to add a high concentration (relative to the concentration of the electroactive species) of supporting electrolyte to the system – common electrochemical practice designed to minimize migration and to minimize uncompensated resistance effects. Bond et al.¹² (see their Figure 7) have examined the effect of increasing the concentration of sup-

**Figure 2.** Plot of $\Delta\rho/\rho$ vs $\log_{10}[c_{\text{SE}}/(1 \text{ mole cm}^{-3})]$. Data details see Table III and associated discussion.

porting electrolyte on the electrochemical reduction of $\text{S}_2\text{Mo}_{18}\text{O}_{62}^{4-}$ to $\text{S}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ and on the density-gradient induced convective current components observed as a function of electrode orientation. The solvent was acetonitrile ($\rho^S = 0.786 \text{ g cm}^{-3}$) and the counter-ions were $(\text{C}_6\text{H}_{13})_4\text{N}^+$ and ClO_4^- . For clarity, we treat this as a 5-species problem to distinguish the analyte related species ($j = 1, 2$ and 3) from the added supporting electrolyte species ($j = 4$ and 5). We approximate relevant G_j -values by M_j/ρ^S for all species involved (see Eq. 37). Thus $G_1 = G_2 = M_{\text{S}_2\text{Mo}_{18}\text{O}_{62}^{4-}}/\rho^S = M_{\text{S}_2\text{Mo}_{18}\text{O}_{62}^{6-}}/\rho^S = 2783/0.786 = 3541 \text{ cm}^3/\text{mole}$, $G_3 = G_5 = M_{(\text{C}_6\text{H}_{13})_4\text{N}^+}/\rho^S = 355/0.786 = 452 \text{ cm}^3/\text{mole}$ and $G_4 = M_{\text{ClO}_4^-}/\rho^S = 99/0.786 = 126 \text{ cm}^3/\text{mole}$. The Δc_j -values were computed as described earlier; then $\Delta\rho/\rho^S$ were computed from Eq. 35 for various concentrations of the supporting electrolyte. The remaining parameters values are summarized in Table III. Note that in the absence of any supporting electrolyte (Table IIIA) $\Delta\rho/\rho^S = -8.83e-4$. Then, as the concentration of the supporting electrolyte is increased (Tables IIIB–IIIE) the value of $\Delta\rho/\rho^S$ increases, actually passing through zero and leveling off at $\sim 3e-4$ (see Figure 2). When $\alpha_D = 0.999999$ this result appears to be qualitatively consistent with the results of Bond et al. (their Figure 7),¹² notably that the density-gradient-induced current effect decreases with increasing concentration of the supporting electrolyte. Figure 2 also suggests that a properly selected supporting electrolyte concentration and a specific value of α_D will eliminate density differences. It is important to keep in mind that $\Delta\rho/\rho^S$ values will be sensitive to non-equality of the diffusion coefficients for the $\text{S}_2\text{Mo}_{18}\text{O}_{62}^{4-}$, $\text{S}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ and counter-ion moieties.

Conclusions

What can be concluded from these analyses?

Our application of the principle of unchanging total concentration¹ allows us to establish the electrochemically induced changes in the concentrations of all species at an electrode surface given a fixed ratio of the redox species at the electrode surface, $c_2^{x=0}/c_1^{x=0}$, and given that the diffusion coefficients of all species are identical. There will be no density gradient in the vicinity of the electrode surface if all species have the same G_j -values – the G_j -value for a given moiety can be computed using the linearized Millero expression (see Eqs. 31 and 32) and known values of the solvent density, ρ^S , molecular mass, M_j , and the standard partial molar volumes, β_j , as compiled by Marcus and coworkers, for example^{14,15} (see Eq. 37).

The most difficult challenge is to quantify the effect of density gradients on the currents produced by the electrochemical perturbation. That is a complicated analysis which involves many factors: e.g., shape and size of the electrode, the orientation of the electrode relative to the gravitational field,^{10,12} the time-scale of the experiment and the electrochemical protocol as discussed in some recent publications.^{4,7}

However, we suggest that even the qualitative analysis offered in the present work can help to clarify some of the key factors involved in electrochemically-induced convection.

Quantification of spontaneous convection as defined by Amatore et al.³ may be facilitated if density-gradient-induced convection and vibration-induced convection can be relatively suppressed (compared to the contribution from spontaneous convection). One simple ploy to at least partially accomplish that objective is by proper adjustment of the orientation of the electrode relative to the gravitational field^{10,12} as well as reducing the size (e.g., the radius) of the electrode, and/or reducing the time-scale of the experiment so that convection has not had time to have an effect as discussed in some recent publications.^{4,7}

A fanciful (albeit costly) way to virtually eliminate density-gradient induced convection is to execute experiments in a zero-gravity or micro-gravity environment. If vibration can be also be suppressed only Amatore's³ spontaneous convection remains.

Acknowledgment

SWF thanks John Miller and the Chemistry Department, Brookhaven National Laboratory, for support of his guest appointment; Henry White, Martin Edwards, Kim McKelvey, Hugh Isaacs and Irina Svir are also thanked for helpful comments and suggestions. ERL was supported by the U.S. Department of Energy's Atmospheric System Research Program (Office of Science, OBER) under contract

DE-SC00112704. This work is dedicated to our colleague Prof. Allen J. Bard with all best wishes.

References

1. K. B. Oldham and S. W. Feldberg, *J. Phys. Chem. B*, **103**, 1699 (1999).
2. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications Second Edition*, John Wiley & Sons, New York (2001).
3. C. Amatore, S. Szunerits, L. Thouin, and J.-S. Warkocz, *J. Electroanal. Chem.*, **500**, 62 (2001).
4. K. Ngamchuea, S. Eloul, K. Tschulik, and R. G. Compton, *Anal. Chem.*, **87**, 7226 (2015).
5. C. Amatore, C. Pebay, L. Thouin, and A. F. Wang, *Electrochem. Comm.*, **11**, 1269 (2009).
6. C. Amatore, C. Pebay, L. Thouin, A. F. Wang, and J.-S. Warkocz, *Anal. Chem.*, **82**, 6933 (2010).
7. V. Sahore, A. Kreidermacher, F. Z. Khan, and I. Fritsch, *J. Electrochem. Soc.*, **163**, H3135 (2016).
8. I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).
9. S. M. Drew, R. M. Wightman, and C. A. Amatore, *J. Electroanal. Chem.*, **317**, 117 (1991).
10. X. Gao, J. Lee, and H. S. White, *Anal. Chem.*, **67**, 1541 (1995).
11. A. M. Bond and S. W. Feldberg, *J. Phys. Chem. B*, **102**, 9966 (1998).
12. A. M. Bond, D. C. Coomber, S. W. Feldberg, and T. Vu, *Anal. Chem.*, **73**, 352 (2001).
13. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran: The Art of Scientific Computing Second Edition*, Cambridge University Press (1994).
14. Y. Marcus, *J. Chem. Soc., Faraday Trans.*, **89**, 713 (1993).
15. Y. Marcus, G. Hefter, and T.-S. Pang, *J. Chem. Soc. Faraday Trans.*, **90**, 1899 (1994).
16. F. J. Millero, *Chem. Rev.*, **61**, 147 (1971).
17. V. D. Kiselev, L. N. Potapova, H. A. Kashaeva, and A. I. Konovalov, *Mendeleev Commun.*, **22**, 50 (2012).